

The University of Chicago

I. CHLORINATION OF BICYCLIC ALIPHATIC  
HYDROCARBONS

II. BROMINE OXIDE IN BROMINATION  
REACTIONS

A DISSERTATION SUBMITTED TO THE FACULTY  
OF THE DIVISION OF THE PHYSICAL SCIENCES  
IN CANDIDACY FOR THE DEGREE OF DOCTOR  
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY  
JUNE, 1945

By  
PERCY B. POLEN

CHICAGO, ILLINOIS

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#### ACKNOWLEDGMENT

The author wishes to express sincerest appreciation to Professor M. S. Kharasch for his invaluable guidance and encouragement during the course of this investigation.



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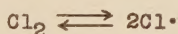
## PART I

### CHLORINATION OF BICYCLIC ALIPHATIC HYDROCARBONS

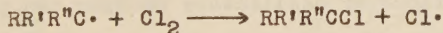
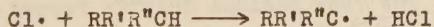
#### INTRODUCTION

There is already available much experimental evidence to support the hypothesis that substitution of hydrogen in saturated aliphatic hydrocarbons by chlorine is a chain reaction.<sup>1</sup> Each of the reactions in the chain is believed to involve free radicals, i.e., neutral atoms or molecules with an unpaired electron. The whole chain (with the exception of the first and last steps) is regarded as a repetition of a unit cycle of reactions. In each of these cycles, a free radical reacts with a molecule to form a new free radical and a new molecule. In chlorination reactions, the chains are initiated by the formation of neutral chlorine atoms from chlorine molecules, and are perpetuated by the generation of a chlorine atom in each of the aforementioned unit cycles.<sup>2</sup>

The assumption of a free-radical-chain mechanism for chlorination leaves open the choice between the two alternative reaction mechanisms indicated below.



#### Mechanism A:

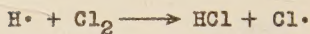
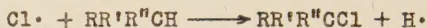


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<sup>1</sup>Pease and Walz, J.A.C.S., **53**, 3728 (1931).

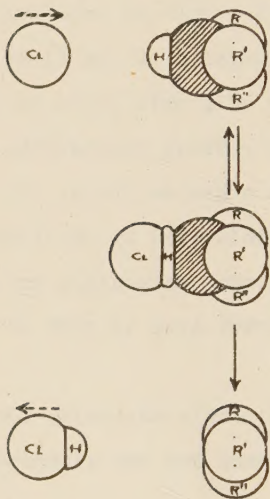
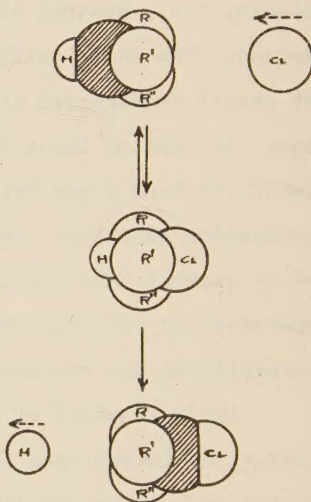
<sup>2</sup>Kharasch and Brown, J.A.C.S., **61**, 2142 (1939); Brown, Kharasch and Chao, ibid., **62**, 3435 (1940).



Mechanism B:

By either mechanism, molecular chlorine acts as the chlorinating agent, and the tertiary aliphatic hydrocarbon,  $\text{RR}'\text{R}''\text{CH}$ , is the substance chlorinated. A dot represents an unpaired electron; R represents an aliphatic radical.

The modes of attack by the chlorine atom in these alternative mechanisms are as follows:

Mechanism AMechanism B

There is evidence<sup>1</sup> which makes mechanism A more probable than mechanism B. The free radical  $\text{RR}'\text{R}''\text{C}\cdot$  formed in mechanism A would be either planar or oscillatory between two pyramidal forms. In either case, in the reaction yielding the alkyl halide, the

<sup>1</sup>Kharrasch and Brown, op. cit.



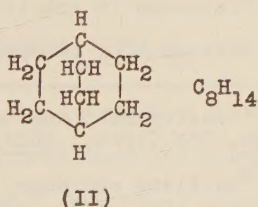
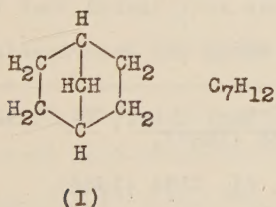
chlorine molecule would approach the free radical with equal probability from either of two directions. If the tertiary carbon in the original hydrocarbon is asymmetric, then the product should be a racemic mixture of the two enantiomorphic forms of a tertiary alkyl halide. On the other hand, under the same conditions, mechanism B should lead to a Walden inversion. The evidence in favor of mechanism A was obtained by chlorinating optically active 1-chloro-2-methyl-butane,  $\text{CH}_3\text{CH}_2\overset{\text{H}}{\underset{\text{CH}_3}{\text{C}}}\text{CH}_2\text{Cl}$ . Among the

products of the reaction was the inactive (dl) 1,2-dichloro-2-methyl-butane,  $\text{CH}_3\text{CH}_2\overset{\text{Cl}}{\underset{\text{CH}_3}{\text{C}}}\text{CH}_2\text{Cl}$ . This product should be obtained if the chlorination proceeds by mechanism A; if the chlorination had proceeded by mechanism B, only one optically active form of this same compound should have been produced.

#### DISCUSSION OF THEORY AND METHOD

The present investigation was undertaken to obtain further evidence bearing on the mechanism of chlorinations by the free-radical-chain mechanism.

Bicyclo-(2,2,1)-heptane (I) and bicyclo-(2,2,2)-octane (II), by virtue of their structure cannot undergo inversion about their tertiary carbon atoms without rupturing a carbon-to-carbon bond.



These tertiary carbon atoms are frequently called "bridge-head" carbon atoms, and the hydrogen or chlorine atoms bonded to them are referred to as "bridge-head" hydrogen or chlorine atoms respectively.

In the chlorination of either of these bicyclic compounds, the formation of a tertiary halide would in itself be evidence for mechanism A. Mechanism B would here involve the penetration of a chlorine atom into the cage-like structure of the carbon skeleton--an exceedingly improbable event. That is to say, if either of these bicyclic compounds were chlorinated, the yield of tertiary halide would be expected to be zero if the chlorination could proceed according to mechanism B only. On the other hand, mechanism A would be expected to yield considerable amounts of tertiary halide, since chlorine usually replaces tertiary hydrogen atoms more easily than it does secondary ones.<sup>1</sup> The actual yield of tertiary halide should, however, be influenced by the ratio between the number of tertiary hydrogen atoms and the total number of hydrogen atoms in the molecule.

Bartlett and Knox<sup>2</sup> have shown that bridge-head halogen atoms do not react with such reagents as alcoholic silver nitrate, alkali hydroxide, etc., even when treated with these reagents for long periods. The secondary monohalides formed from bicycloheptane and bicyclo-octane react readily (see experimental part) with these reagents to lose all of their halogen. In view of these differences in reactivity, it was anticipated that the presence or absence of a tertiary halide among the chlorination prod-

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<sup>1</sup>Hass, McBee, and Weber, Ind. Eng. Chem., 27, 1190 (1935); ibid., 28, 333 (1936); ibid., 29, 1335 (1937).

<sup>2</sup>Bartlett and Knox, J.A.C.S., 61, 3184 (1939).

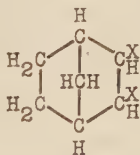
ucts of the two bicyclic compounds under consideration could be demonstrated. If the chlorine content of these products were determined first by combustion (Parr bomb) and then by hydrolysis (silver nitrate or potassium hydroxide), any difference between the two results should correspond to the amount of tertiary halide present.

The success of the method just described depends upon the correctness of two assumptions, neither of which appeared at first to be improbable. These two assumptions are as follows:

1. That the reaction products are all monohalogen isomers, or that, if appreciable quantities of polyhalogen derivatives are formed, the individual halogen atoms in these derivatives react independently of one another.
2. That, if bicyclic free radicals are formed during the course of the reaction they do not disproportionate (as many free alkyl radicals have been shown to do), but instead, react according to the equation



The presence of a bicyclic alkene (e.g., bicycloheptene-2) in the reaction mixture would lead to the formation of a 2,3-dihalide of the type



It is very difficult if not impossible to remove all of the halogen from such dihalides merely by hydrolysis. (See experimental part).

#### DISCUSSION OF EXPERIMENTAL RESULTS

In preliminary experiments, the reactivity of the chlorine atoms in 2-chloro-bicyclo-(2,2,1)-heptane and 2-chloro-bicyclo-(2,2,2)-octane was determined. From these compounds, the halogen is removed quantitatively by treatment either with



silver nitrate in aqueous t-butanol at 80° or with potassium hydroxide in diethylene glycol at 120°. Consequently, if a mixture of monochlorinated derivatives of either of the two hydrocarbons in question contains chlorine which is not removed by hydrolysis under the conditions cited, that chlorine must be attached to the tertiary carbon atoms.

In the experiments here recounted, in order to avoid polychlorination of the hydrocarbons, the amount of chlorine added to the solution of the hydrocarbon was less than the theoretical amount required for the formation of a monohalide. It should be noted, however, that the amount of tertiary chlorine is determined by a difference between two analyses. Unless the amount of tertiary substitution is considerable, this difference falls within the experimental error of the analytical methods used. Halogenation on a tertiary carbon atom is usually more rapid than halogenation on a secondary, but, in the hydrocarbons in question, the ratios between the numbers of tertiary and secondary carbon atoms are two to ten and two to twelve respectively. Consequently, the probability of the formation of a secondary alkyl halide is increased. Since no great confidence was placed on calculations dealing with such a complicated situation, the optimum amount of chlorine to be added was determined empirically. It turned out that 50% to 75% of the theoretical amount of chlorine necessary for the formation of a monohalide gave very satisfactory results.

The chlorinations of the two hydrocarbons were carried out either photo-chemically or with sulfuryl chloride, using benzoyl peroxide as a catalyst. The crude products obtained, when analyzed for chlorine by either the combustion or the hydrolysis method gave reproducible results.

Efforts to separate the components of these crude products

met with little success because of the strong tendency of some of the components to sublime. When the attempt was made to distill such mixtures, materials which tended to solidify in the column came over along with liquid fractions. Moreover, the temperature read on the thermometer in the still-head varied widely with small changes in the rate of heating. The figures from one such distillation of a mixture obtained by the chlorination of bicyclo-(2,2,1)-heptane are given in Table 1.

Before discussing the results set forth in that table, it is necessary to define the term "degree of chlorination" which appears there. The degree of chlorination is the average number of chlorine atoms per molecule in the crude reaction product from which free chlorine and hydrochloric acid have been removed. That is to say, since the hydrocarbon of formula  $C_7H_{12}$  was used in this instance, a fraction of the distillate containing 27.15% chlorine (corresponding to the formula  $C_7H_{11}Cl$ ) would be said to have one for its degree of chlorination; a fraction containing 42.86% chlorine (corresponding to the formula  $C_7H_{10}Cl_2$ ) would be said to have two for its degree of chlorination. Any fraction with a chlorine content between 27.15% and 42.86% would have a number between one and two for its degree of chlorination. Obviously, this calculation is based on the assumption that no dimerization of the carbon skeleton occurs during the reaction. As a matter of fact, no evidence indicating such dimerization was found. The degree of chlorination,  $n$ , for any fraction may be calculated from the weight per cent of chlorine,  $x$ , by the following formulas:

$$\text{For bicyclo-(2,2,1)-heptane: } n = \frac{96.10x}{3546 - 34.46x}$$

$$\text{For bicyclo-(2,2,2)-octane: } n = \frac{110.11x}{3546 - 34.46x}$$

TABLE 1

FRACTIONS OBTAINED BY DISTILLING PRODUCT<sup>a</sup> FROM PHOTO-CHLORINATION  
OF BICYCLO-(2,2,1)-HEPTANE

| Frac-<br>tion | Temperature<br>C. | Pressure<br>mm. of Hg | Form | Weight<br>Grams | n <sub>D</sub> <sup>20</sup> | M.P.<br>C.       | % Cl (Wt. basis) |                   | Degree of<br>Chlorina-<br>tion |
|---------------|-------------------|-----------------------|------|-----------------|------------------------------|------------------|------------------|-------------------|--------------------------------|
|               |                   |                       |      |                 |                              |                  | Parr Bomb        | AgNO <sub>3</sub> |                                |
| #1            | <80°              | 750                   | Liq. | 1.1             | 1.3858                       | .....            | ....             | ....              | .....                          |
| #2            | 76°-82°           | 300                   | Sol. | 1.4             | .....                        | 84° <sup>c</sup> | ....             | ....              | { 0.10 }                       |
| #3            | 82°-88°           | 300                   | Sol. | 4.6             | .....                        | 75°-6°           | 3.6              | 3.2               |                                |
| #4            | 76°-88°           | 300                   | Sol. | 2.0             | .....                        | 73°-5°           | ....             | ....              |                                |
| #5            | 119°-129°         | 300                   | Liq. | 16.4            | 1.4840 <sup>b</sup>          | .....            | ....             | ....              | ca. 1.00                       |
| #6            | 106°              | 150                   | Liq. | 2.4             | 1.4840 <sup>b</sup>          | .....            | ....             | ....              | ca. 1.00                       |
| #7            | 46°-54°           | 11                    | Liq. | 1.3             | 1.4851 <sup>b</sup>          | .....            | 26.5             | 26.2              | ca. 1.00                       |
| #8            | 79°-85°           | 11                    | Liq. | 8.8             | 1.5090                       | .....            | 41.1             | 20.8              | 1.85                           |
| #9            | .....             | 10 <sup>-4</sup>      | Liq. | 4.3             | .....                        | .....            | 50.0             | 13.1              | 2.63                           |

<sup>a</sup>Degree of chlorination 1.1.<sup>b</sup>n<sub>D</sub><sup>20</sup> of 2-chloro-bicyclo-(2,2,1)-heptane = 1.4840.<sup>c</sup>Melting point of bicyclo-(2,2,1)-heptane 86°.



Table 1 shows that, although the total mixture distilled had a degree of chlorination 1.1, it nevertheless contained about 20% of unchlorinated hydrocarbon and a corresponding amount of polyhalogenated products. If fraction #8 consists entirely of compounds with the formulas  $C_7H_{11}Cl$  and  $C_7H_{10}Cl_2$ , and if fraction #9 consists entirely of compounds with the formulas  $C_7H_{10}Cl_2$  and  $C_7H_9Cl_3$ , then the unchlorinated hydrocarbon represents about 23 mole per cent of the total mixture. An estimate (based on figures in Table 1) of the yields of various classes of compounds in the reaction is given in Table 2.

TABLE 2

ESTIMATED MOLE FRACTIONS OF HALIDES IN PRODUCT  
FROM CHLORINATION OF BICYCLO-(2,2,1)-HEPTANE\*

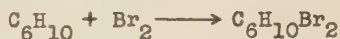
| Compounds of<br>formula | Mole Fraction |
|-------------------------|---------------|
| $C_7H_{12}$ .....       | 0.231         |
| $C_7H_{11}Cl$ .....     | 0.544         |
| $C_7H_{10}Cl_2$ .....   | 0.180         |
| $C_7H_9Cl_3$ .....      | 0.046         |
| Total .....             | 1.001         |

\*Calculated from Table 1. Fraction #1 excluded.

The presence among the reaction products of considerable amounts of polyhalogen derivatives raised some new questions. It had never been determined whether all the secondary halogen in the various possible dihalogen derivatives of bicyclo-heptane can be removed by hydrolysis under the conditions already described. An attempt was made to throw light on these questions first by model hydrolyses of 1,2-dichloro- and 1,2-dibromocyclohexane and then by further hydrolysis experiments on the

2,3-dichloro- and 2,3-dibromo-derivatives of bicyclo-heptane.

Cyclohexene in one-tenth molar or in one molar solutions in glacial acetic acid, when treated with bromine under various conditions, in all instances absorbed the amount of bromine demanded by the equation



There was probably no substitution of hydrogen by bromine, for no hydrobromic acid could be detected in the reaction products. From some of the products thus obtained, the 1,2-dibromo-cyclohexane was isolated. This was dissolved in t-butanol (80°) or diethylene glycol (120°) and treated with silver nitrate or potassium hydroxide respectively. The silver nitrate removed only about 19% of the bromine in 48 hours; the potassium hydroxide removed all the bromine in less than five hours. In a similar set of experiments, 1,2-dichloro-cyclohexane was prepared and hydrolyzed. The results were practically identical with those obtained from the bromine derivative. Potassium hydroxide, under the conditions cited for that reagent, rapidly removed all of the chlorine from the molecule; silver nitrate, under the conditions cited for that reagent, proved ineffective.

Bicyclo-heptene in glacial acetic acid was treated with chlorine under conditions which should lead only to saturation and not to substitution--that is, the amount of chlorine used was only about one-half of the amount required by the equation



This amount was readily absorbed. No attempt was made to isolate the products formed. Instead, the acetic acid together with any chlorine or hydrochloric acid which may have been present were removed from the reaction product; then the mixture of hydrocarbon and halogenated derivatives was submitted to hydrolysis.

Of the total amount of halogen absorbed (as determined by combustion methods) only about 80% was removed even by prolonged treatment (48 hours) with potassium hydroxide or silver nitrate under the respective conditions already cited. Similar results were obtained when bromine was added to the bicyclo-heptene. Here again only about 80% of the added halogen could be removed by hydrolysis. No corresponding set of experiments was carried out with bicyclo-octene.

It is evident from the experiments just cited that at least part of the chlorine or bromine in the reaction products formed by the addition of halogen to bicyclo-heptene is much more firmly bound than are the halogen atoms in 1,2-dichloro- or 1,2-dibromo-cyclohexane. At first, it was surmised that the addition of the halogen might have been accompanied by some substitution on the tertiary carbon atom, and that it was the bridge-head halogen which proved resistant to hydrolysis. The fact that no free hydrogen halide was noticed in the reaction products decreased the probability of this explanation, but the small amount of hydrogen halide formed might have escaped detection. Consequently, an attempt was made to determine whether, in the addition of bromine to the bicyclo-heptene, the amount of bromine absorbed was greater than that demanded by the equation

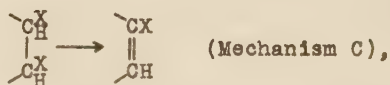


When the bromination was carried out in dilute (0.1 molar) glacial acetic acid solution, the amount of bromine absorbed corresponded accurately with the amount demanded by the above equation. The end point of the bromination was very sharp, and if excess bromine was added, the amount of this excess reagent remained unchanged even when the mixture was allowed to stand for nineteen hours. These facts make it improbable that during the addition

reaction to the double bond, any substitution on the tertiary carbon atom takes place.

When the bromination was carried out exactly as above, except that a 1.0 molar solution of the hydrocarbon in glacial acetic acid was used, the end point was again very sharp, and excess bromine was not absorbed even when the mixture stood nineteen hours. But curiously enough, the amount of bromine absorbed corresponded to only 73% of the amount demanded by the equation.

On the basis of the results just described, no fully satisfactory explanation for the unreactive character of part of the halogen in the dihalogen derivatives of bicyclo-heptane can be advanced. The assumption of substitution on the tertiary carbon atom is not justified. If the first step of the hydrolysis reaction were

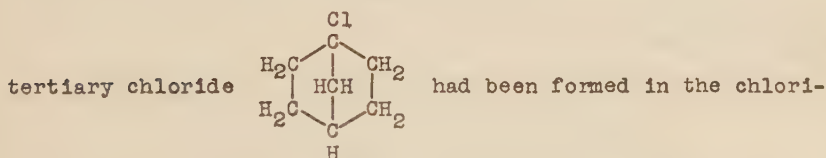
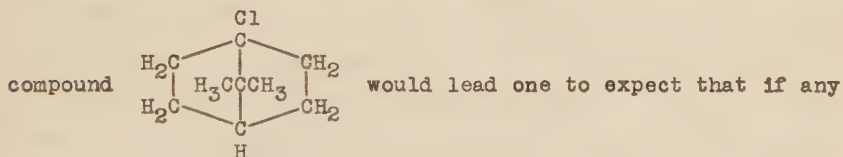


then the product of this reaction would be an alkyl halide of the type of the vinyl halides, from which, as is well known, the halogen can be removed only with great difficulty. But if the entire hydrolysis proceeds by the mechanism just suggested, exactly half of the halogen absorbed should be removable, whereas, as a matter of fact, about 80% is removed by either of the two reagents used. It is conceivable that the hydrolysis might run to the extent of 40% by mechanism C and to the extent of 60% by some other mechanism in which no monohalide of the vinyl type occurs as an intermediate. This assumption would account for the results obtained, but there is no other evidence in its favor. Moreover, the fact that both silver nitrate and potassium hydroxide remove almost exactly the same amounts of halogen makes this



hypothesis less probable. The mechanisms by which these two reagents bring about hydrolysis are frequently quite different from one another. It is hardly likely that in this particular instance they should both drive the reaction to the extent of 40% along one path and to the extent of 60% along another.

In the light of these considerations, the findings given in Tables 1 and 2 may be discussed. Fractions #5, #6 and #7 are probably nearly pure 2-chloro-bicyclo-heptane, since the physical constants of these fractions agree quite closely with those of material prepared by the addition of hydrogen chloride to bicyclo-heptene. From these fractions all of the chlorine is readily removed by hydrolysis. The properties of Bartlett and Knox's<sup>1</sup>



nation here under discussion, this tertiary chloride should occur in fractions #2 to #4 rather than in fractions #8 to #9. But all the halogen in fractions #2 to #4 is easily removable by hydrolysis. Hence, if Bartlett and Knox's thesis that bridge-head halogen atoms cannot be removed by hydrolysis is correct, it must be concluded that, in the present reaction, no tertiary monochloride was formed. This finding clearly indicates that, in the two hydrocarbons studied, the tertiary hydrogen atoms

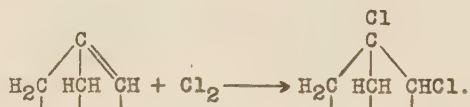
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<sup>1</sup>Ibid.

(contrary to the usual rule) are less reactive (at least so far as substitution by chlorine is concerned) than the secondary ones. It is noteworthy that the tertiary monochloride with which Bartlett and Knox experimented was not prepared by the direct chlorination of the corresponding hydrocarbon.

Whether the reversal of the order of reactivity here noted is associated with the impossibility of replacing the tertiary hydrogen according to mechanism B is a question which may be left open.

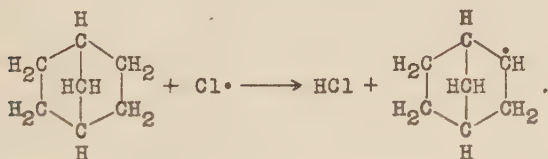
The compounds composing fractions #8 and #9 are mostly dichlorides and trichlorides. About 59% of the chlorine in these fractions cannot be removed by hydrolysis. The experiments previously described indicate that it would be unsafe to assume that all of the non-hydrolyzable chlorine is tertiary. The question whether any of it is tertiary remains to be discussed. Since double bonds to bridge-head carbon atoms probably cannot be formed, tertiary chlorine cannot be accounted for by the intermediate reaction



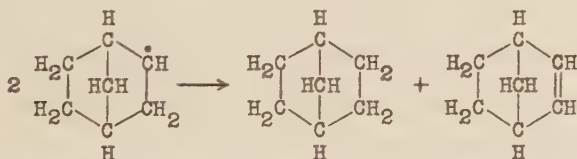
If there is any tertiary chlorine present in fractions #8 and #9, the compound containing such halogen must have been formed by the substitution by chlorine of a bridge-head hydrogen atom in a compound such as 2-monochloro- or 2,3-dichloro-bicycloheptane. This mode of formation is, however, improbable. In the hydrocarbons themselves the tertiary halogen atoms have been shown to be less reactive than the secondary ones. It is difficult to see why the introduction of one or more secondary halogen atoms should reverse the order of reactivity between the tertiary

hydrogen atoms and the secondary hydrogen atoms still present in the molecule. Consequently, it seems probable that none of the unhydrolyzable chlorine in fractions #8 and #9 is tertiary. That not all of the chlorine in 2,3-dichloro-bicyclo-heptane is removable by hydrolysis has already been demonstrated.

It remains to consider the significance of the large amount of unchanged hydrocarbon found in the product dealt with in Table 1. As has already been shown, the first steps in the chlorination reaction are probably

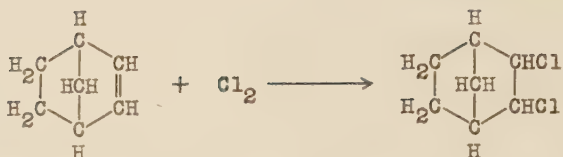


The presence of a large amount of hydrocarbon in the reaction product probably indicates that at least part of the free radical thus formed disproportionates.



Thus, assumption #2 (see page 5) is very probably unjustified. It should be noted that all the halogenations here described were carried out in such a manner that the chlorine content of the reaction mixture was at all times very low, a condition under which disproportionation of the free radical is particularly facilitated.

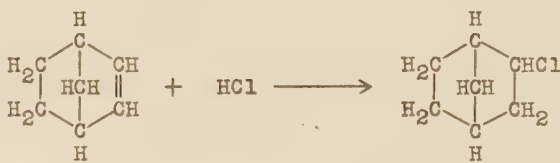
The large amount of dihalogen derivative in the reaction product is probably formed by the addition of chlorine to the bicyclo-heptene formed by disproportionation.



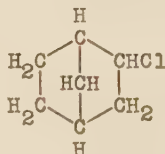
Perhaps some part of the monohalogen derivative found is not formed by the reaction



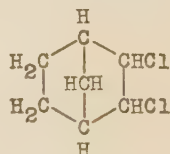
but rather by the addition of hydrogen chloride to bicycloheptene



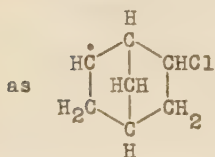
Very probably the molecules



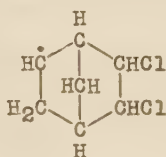
and



react again with free chlorine atoms to give free radicals such

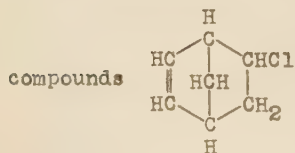


or

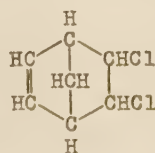


These would again

tend to disproportionate to yield respectively the unsaturated



and

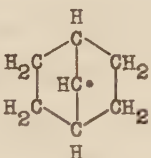


These, by



addition of chlorine, would give the tri- or tetra-halogenated derivatives, some of which must be present in fraction #9. If the polyhalides present in fractions #8 and #9 are of the types indicated then assumption #1 (page 5) is erroneous, for all of the chlorine in 2-chloro-bicyclo-heptane is removed by hydrolysis, whereas part of the chlorine in the polyhalides cannot be thus removed.

Throughout the work here recounted no evidence for the

formation of a secondary free radical  was observed.

Evidently this radical could not disproportionate directly. It might, however, first rearrange and then disproportionate.

It was originally intended to halogenate bicyclo-octane and to fractionate the reaction product in the manner shown in Table 1 for bicyclo-heptane. However, the difficulties in preparing large quantities of bicyclo-octane prevented the carrying out of this program within the time available. All that was ever done with bicyclo-octane was to chlorinate it with small amounts (less than 1 mole) of chlorine and to determine the proportion of hydrolyzable chlorine in the crude reaction products. This varied between 85% and 90% depending upon the degree of chlorination. Since all of the chlorine in 2-chloro-bicyclo-octane hydrolyzes easily, the presence of unhydrolyzable chlorine in the reaction products just mentioned probably indicates the presence of some 2,3-dichloride in this material. All of the fragmentary evidence available tends to show that the halogenations of bicyclo-heptane and bicyclo-octane proceed in very much the same way. Unfortunately, the present incomplete treatment of these two

reactions leaves open a number of questions with regard to their mechanisms.

## EXPERIMENTAL PART

### Preparation and Source of Materials

#### Bicyclo-(2,2,1)-heptene-2 and Bicyclo-(2,2,1)-heptane.--

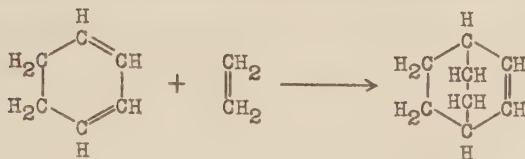
Generous quantities of both bicyclo-(2,2,1)-heptene-2 and bicyclo-(2,2,1)-heptane were furnished by Dr. C. L. Thomas of the Universal Oil Products Company. The heptene melted (sealed tube) at 46° (uncorrected); the heptane melted (sealed tube) at 86°-87° (uncorrected). These melting points agree with those reported in the literature.<sup>1</sup>

Additional bicyclo-heptane was prepared by hydrogenating some of the bicyclo-heptene-2 in the presence of platinum oxide catalyst at room temperature and an initial hydrogen pressure of about four atmospheres; ethyl alcohol (95%) was used as a solvent. The theoretical amount of hydrogen was absorbed in less than one hour. After the catalyst had been removed by filtration from the crude reaction product, the hydrocarbon was precipitated from the filtrate by addition of water. The precipitate was collected on a suction filter, and partially dried on filter paper. It was finally sublimed from a bed of anhydrous calcium chloride. The yield of sublimed material was about 80% of the amount calculated. The compound thus prepared melted (sealed tube) at 86°-87° (uncorrected).

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<sup>1</sup>Joshell and Butts, J.A.C.S., 63, 3350 (1941); Kompa and Beckman, Ann., 512, 184 (1934); Alder and Richert, Ann., 543, 1 (1939).

Preparation of Bicyclo-(2,2,2)-octene-2.--



Thirty-five grams of 1,3-cyclohexadiene, prepared by the method of Kistiakowsky et al,<sup>1</sup> was placed in a high pressure hydrogenation bomb. One-tenth gram of hydroquinone was added as an anti-oxidant. Ethylene was passed directly from a commercial cylinder into the mixture until the pressure in the bomb was about 900 pounds per square inch. Then the bomb was rocked for one-half hour to insure physical saturation of the liquid by the gas. The system was closed off and heated electrically to 180° for eighteen hours. After about two hours, a maximum pressure of 2900 to 3000 pounds per square inch was reached; thereafter the pressure dropped slowly to about 2600 pounds per square inch where it remained as long as the heating was continued.

After the apparatus had cooled to room temperature, the excess gas was released, and the semi-crystalline residue was transferred to a sublimation apparatus. At 40° and a pressure of about 30-40 mm., 22 grams of white needle-like crystals accumulated rapidly on the cold finger. This yield is 47% of the amount calculated on the basis of the cyclohexadiene used. The sublimate was a white, highly volatile solid, with a camphor-like odor. It melted (sealed tube) at 114°-115° (uncorrected). A portion of this material was recrystallized from 70% ethyl alcohol, superficially dried by pressing on filter paper, and finally sublimed from an anhydrous calcium chloride bed. This purified material melted (sealed tube) at 115°. The melting

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<sup>1</sup>Kistiakowsky, Ruhoff, Smith and Vaughan, J.A.C.S., **58**, 146 (1936).

point reported in the literature<sup>1</sup> is 113°-114°.

The total amount of bicyclo-octene-2 produced in the reaction described probably exceeds the 47% yield reported. This compound like other solid substances in the bicyclo-(2,2,2)-octane and the bicyclo-(2,2,1)-heptane series is highly volatile. It disappears rapidly at ordinary temperatures and pressures if not carefully kept in closed containers.

Preparation of Bicyclo-(2,2,2)-octane.-- To 4 grams of bicyclo-(2,2,2)-octene-2 dissolved in 50 cc. of 95% ethyl alcohol, 50 mg. of platinum oxide catalyst was added. The mixture was hydrogenated at room temperature in an all-glass hydrogenation apparatus and at an initial hydrogen pressure of 3 atmospheres. The theoretical amount of hydrogen was absorbed in less than one hour. After the catalyst had been removed from the product by filtration, the saturated hydrocarbon was precipitated from the filtrate by the addition of water. The precipitate was rapidly collected on a suction filter, superficially dried with filter paper, and sublimed from anhydrous calcium chloride at reduced pressure. The product, bicyclo-octane was a highly volatile, white, crystalline solid which melted (sealed tube) at 173° (uncorrected).<sup>2</sup>

Cyclohexene.-- Commercial cyclohexene was fractionated through a 30 cm. column with a spiral nichrome wire packing. The fraction boiling at 82.5°-83.5° was collected and stored in a brown glass-stoppered bottle.

Preparation of 2-Chloro-bicyclo-(2,2,1)-heptane.-- Bicyclo-(2,2,1)-heptene-2 (22 grams) was dissolved in about 30 cc.

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<sup>1</sup>Seka and Tromposch, Ber., 75B, 1379 (1942); Chem.Abstr. 37, 4723 (1943).

<sup>2</sup>Kompa and Beckman, Ann., 512, 184 (1934).



of glacial acetic acid containing a trace of ferric chloride. Dry hydrogen chloride gas was passed into the solution until the increase in weight corresponded to 1.8 moles of hydrogen chloride per mole of heptene used. The solution was then allowed to stand over night. Water (about 75-100 cc.) was added, whereupon two layers separated. The oily layer was washed several times with a 5% solution of sodium carbonate and finally with water. It was then dried with anhydrous calcium chloride and distilled at reduced pressure. A fraction boiling at  $47^{\circ}$ - $50^{\circ}$ /11 mm. was collected. This boiling point agrees with that given in the literature.<sup>1</sup> The amount of product obtained was 23.5 grams (77% of the theoretical yield). The refractive index was  $n_D^{20} = 1.4840$ .

Preparation of 2-Chloro-bicyclo-(2,2,2)-octane.--

Resublimed bicyclo-(2,2,2)-octene-2 (5.5 grams) was dissolved in 50 cc. glacial acetic acid. The material was placed in a glass bomb, and dry hydrogen chloride gas was passed into the mixture until the solution was thoroughly saturated and practically all of the air had been displaced from the bomb. The bomb was cooled in liquid nitrogen, and dry hydrogen chloride was added (with the delivery tube above the surface of the solid) until the amount of solidified hydrogen chloride corresponded to about 4.3 moles per mole of hydrocarbon used. The bomb (still immersed in liquid nitrogen) was evacuated to remove any liquid oxygen which might have condensed in the system; then it was sealed at a pressure of 40 mm. The bomb was heated to  $40^{\circ}$ - $45^{\circ}$  for three hours. Then it was cooled and allowed to remain at room temperature over night. The contents were then removed and diluted with water. The solid which precipitated was rapidly collected on a suction filter,

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<sup>1</sup>Alder and Richert, op. cit.

washed first with a 5% solution of sodium bicarbonate and then with water, and finally pressed on filter paper. The moist solid was then sublimed from a bed of anhydrous calcium chloride. The yield of sublimed material was 4 grams, 54% of the amount calculated. A portion of this material was recrystallized from 70% ethyl alcohol and resublimed. It melted (sealed tube) at  $110^{\circ}$  (uncorrected). The product was a volatile white, waxy solid. Analysis by the Parr bomb method showed it to contain 23.85% of chlorine. The theoretical chlorine content is 24.54%.

Attempts to prepare 2-chloro-bicyclo-octane at atmospheric pressure by treating acetic acid solutions of bicyclo-(2,2,2)-octene-2 with hydrogen chloride at zero degrees or room temperature (with or without ferric chloride as a catalyst) gave unsatisfactory results. The chlorine content of the products thus obtained was about 85-92% of the amount demanded by theory.

#### Addition of Halogens to Unsaturated Hydrocarbons

##### Addition of Halogens to Bicyclo-(2,2,1)-heptene-2.--

An approximately 1 molar solution of bicyclo-(2,2,1)-heptene-2 (10 grams) in glacial acetic acid was placed in a flask surrounded by an ice bath. The desired amount of commercial chlorine was condensed into a graduated trap immersed in a bath of dry ice and methanol; then the chlorine was allowed to evaporate and pass into the solution. About one-half the amount of chlorine required for complete saturation was used. The entire reaction was carried out with the apparatus protected from light. After the mixture had stood about one hour, water (100 cc.) was added. The oil which separated was washed first with dilute sodium carbonate solution and then with water. The oil was dried with anhydrous calcium chloride and distilled under reduced pressure.

The addition of bromine to bicyclo-heptene was carried out in the same manner except that an approximately 1 molar solution of bromine in acetic acid was slowly added to the acetic acid solution of the hydrocarbon.

Quantitative Absorption of Bromine by Cyclohexene and Bicyclo-(2,2,1)-heptene-2 in Dilute Solution.-- Samples (about 0.5 gram) of the hydrocarbons were weighed out in 50 ml. volumetric flasks, and glacial acetic acid was added to make the solutions up to volume. The solutions thus prepared were approximately 0.1 molar with respect to the hydrocarbon. A 10 ml. fraction of each solution was transferred to a glass-stoppered bottle and treated either with a standardized solution of bromine in acetic acid or with 0.5 cc. of concentrated hydrochloric acid and a standardized (approximately 0.1 normal) potassium bromate-bromide solution. Approximately 25% more than the theoretical amount of brominating reagent was used. The bottles containing the mixtures thus prepared were immediately placed in the dark and allowed to stand for two hours. (Successive titrations of samples which had been allowed to stand for various lengths of time showed that, after one hour, there was practically no further absorption of bromine.) Then 1.5 grams of potassium iodide and two to three grams of sodium carbonate were added, and the solution was diluted with water to about 100 cc. The excess iodine was immediately titrated (starch indicator) with standardized (approximately 0.1 normal) sodium thiosulfate. The following table gives the amounts of bromine absorbed. These amounts are expressed as per cents of the total amount of bromine which should be absorbed if the saturation were complete and no substitution occurred.

| Substance                     | Determination with<br>$\text{KBr-KBrO}_3$ | Determination with<br>$\text{Br}_2$ in $\text{CH}_3\text{COOH}$ |
|-------------------------------|-------------------------------------------|-----------------------------------------------------------------|
| Cyclohexene                   | 96.0%                                     | 98.5%                                                           |
| Bicyclo-(2,2,1)-<br>Heptene-2 | 101.7%                                    | 100.3%                                                          |

Quantitative Absorption of Bromine by Cyclohexene and Bicyclo-heptene-2 in Concentrated Solution.-- Samples (about 0.5 gram) of the hydrocarbons were weighed in 50 ml. volumetric flasks, and sufficient (about 5 cc.) glacial acetic acid was added to make the solution about one molar with respect to the hydrocarbon. A standardized (about 0.75 molar) solution of bromine in acetic acid was added drop by drop until the color of the bromine remained undischarged for about 30 seconds; then an excess of the bromine solution was rapidly added. The mixture was allowed to stand in the dark. (The concentrated bromine solutions were measured in a graduated pipette operated by means of a water-pump; the pipette was attached to the pump through a three-way stop-cock with one opening to the air. The liquid level in the pipette was adjusted, and liquid was released from the pipette by manipulating the three-way stop-cock. Thus suction by mouth was avoided and the bromine solution never came in contact with any greased joint).

Successive titrations of the solutions showed that practically no further absorption of bromine occurred after 1.5 hours. The solutions were therefore allowed to stand for 2.5 hours. Each was then made up to 50 ml. with glacial acetic acid. Samples (10 ml.) of each solution were treated with potassium iodide and sodium carbonate; the iodine thus liberated was ti-



trated as previously described. Blank determination made with bromine in acetic acid under the conditions just described but in the absence of any hydrocarbon, showed loss of bromine to be negligible.

When these concentrated solutions of the hydrocarbons were used, cyclohexene absorbed 98.2%, whereas bicyclo-heptene-2 absorbed only 73.2% of the theoretical amount of bromine. In a few instances the diluted reaction mixture of bicyclo-heptene-2 was allowed to stand for nineteen hours and then titrated once more. No additional bromine was absorbed during this interval.

#### Chlorinations

Peroxide-catalyzed Chlorinations.-- A trace of benzoyl peroxide was added to an acetyl chloride solution (approximately 1 molar) of bicyclo-heptane or bicyclo-octane. This solution was heated to boiling under reflux condenser, and sulfuryl chloride was slowly added. The quantity of sulfuryl chloride used was less than one mole per mole of hydrocarbon. Boiling under reflux was continued for six hours, at the end of which time all evidence of reaction had ceased. The mixture was cooled to zero degrees and added slowly to an excess of crushed ice. If a solid product separated, it was collected on a filter and washed first with 5% sodium carbonate solution and then with water. It was then partially dried by filter paper and sublimed from a bed of anhydrous calcium chloride. If the product which separated was an oil, it was separated, washed first with 5% sodium carbonate solution, then with water, and dried with calcium chloride. Finally it was distilled at reduced pressure.

Photo-chlorination of Bicyclo-heptane.-- An approximately 1 molar solution of bicyclo-heptane in acetyl chloride was placed

in a 500 cc. reaction flask. The desired amount of commercial chlorine (less than 1 mole of chlorine per mole of hydrocarbon) was condensed into a graduated trap immersed in a bath of dry ice and methanol. This chlorine was then slowly distilled into the acetyl chloride solution which was kept boiling under a reflux condenser while the mixture was illuminated with a 500 watt Mazda bulb placed within 2 to 3 cm. of the reaction flask. The reaction mixture was then cooled to zero degrees and added slowly to crushed ice. The product (solid or liquid) which separated was treated in the same manner as described in the previous paragraph.

#### Analysis for Halogen Content

Analyses for total and hydrolyzable halogen were carried out by the methods hereafter described. The results thus obtained are given in Table 3.

Analyses for Total Halogen Content.-- The Parr bomb method was used in the analyses for total halogen content. A sample of the material to be analyzed was accurately weighed in a gelatine capsule; the filled capsule was heated with an excess of sodium peroxide to cherry-red heat in a sealed steel bomb. The resulting mixture was dissolved in water, acidified with nitric acid and titrated (Volhard) for chloride or bromide ion.

Analyses with Silver Nitrate for Hydrolyzable Halogen.-- Weighed samples of the material to be analyzed (about 0.1 gram) were dissolved in 10 cc. of t-butanol. Two cubic centimeters of water and 0.5 gram of silver nitrate were added to each solution. Most of the reactions were carried out in large test tubes, each of which was equipped with a water-cooled cold-finger which was seated into the test tube by a ground glass joint. The cold-

TABLE 3

COMPARISON OF HALOGEN CONTENT OF VARIOUS PRODUCTS AND COMPOUNDS  
AS DETERMINED BY DIFFERENT METHODS OF ANALYSIS

| Sample                                                                              | Total Halogen<br>Content (%)<br>(Parr Bomb<br>Analysis) | Hydrolytic<br>Reagent                                                                                      | Reaction<br>Time<br>(Hours) | Hydrolyzable<br>Halogen Content<br>(%) | % of Total<br>Halogen<br>Found by<br>Hydrolysis |
|-------------------------------------------------------------------------------------|---------------------------------------------------------|------------------------------------------------------------------------------------------------------------|-----------------------------|----------------------------------------|-------------------------------------------------|
| 2-Chloro-bicyclo-<br>(2,2,1)-heptane                                                | 26.5                                                    | AgNO <sub>3</sub><br>KOH                                                                                   | <24<br><24                  | 26.5<br>26.6                           | 100<br>101                                      |
| 2-Chloro-bicyclo-<br>(2,2,2)-octane                                                 | 24.5                                                    | AgNO <sub>3</sub>                                                                                          | <24                         | 24.7                                   | 101                                             |
| 1,2-Dichloro-<br>cyclohexane                                                        | 43.4                                                    | AgNO <sub>3</sub><br>KOH                                                                                   | 48<br><5                    | 6.5<br>43.4                            | 15<br>100                                       |
| 1,2-Dibromo-<br>cyclohexane                                                         | 64.6                                                    | AgNO <sub>3</sub><br>KOH                                                                                   | 48<br><5                    | 12.3<br>64.6                           | 19<br>100                                       |
| Product mixture #1<br>from addition of<br>chlorine to bicyclo-<br>(2,2,1)-heptene-2 | 29.4                                                    | AgNO <sub>3</sub><br>AgNO <sub>3</sub><br>AgNO <sub>3</sub> (at 25°)<br>AgNO <sub>3</sub> (sealed<br>tube) | 24<br>48<br>24<br>24        | 23.7<br>24.1<br>20.3<br>24.6           | 81<br>82<br>70<br>83                            |
| Product mixture #2<br>from addition of<br>chlorine to bicyclo-<br>(2,2,1)-heptene-2 | 29.3                                                    | AgNO <sub>3</sub> (sealed<br>tube)<br>KOH<br>KOH                                                           | 24<br>24<br>48              | 23.6<br>22.5<br>24.6                   | 80<br>77<br>84                                  |
| Product mixture from<br>addition of bromine to<br>bicyclo-(2,2,1)-<br>heptene-2     | 50.9                                                    | AgNO <sub>3</sub><br>KOH                                                                                   | 24<br>24                    | 40.5<br>37.5                           | 80<br>74                                        |

finger extended into the tube to a point about 1 cm. above the surface of the liquid. A side arm on the test tube (protected by a soda-lime tube) provided for the maintenance of atmospheric pressure within the system. In some instances the reactions were simply carried out in sealed glass tubes. The results obtained by the use of the two forms of apparatus were practically identical. The apparatus was heated to 80° in an oil bath for about twenty-four hours. Successive determinations carried out on samples of the same substance showed that the per cent of silver chloride formed remained practically constant after this period. The amount of silver chloride was determined gravimetrically by a semi-micro technique.

Analysis with Potassium Hydroxide for Hydrolyzable

Halogen.-- The hydrolytic reagent, 1 normal potassium hydroxide in diethylene glycol, was prepared according to the directions of Shriner and Fuson.<sup>1</sup> Each sample of halide (about 0.2 grams) was weighed in a small glass bomb. About 5 cc. of the reagent was then added. The bomb was surrounded by an ice-bath and sealed off at a pressure of about 40-50 mm. The sealed bomb was completely immersed in an oil-bath heated to 120° ( $\pm 5^\circ$ ). The bomb was kept at this temperature until successive analyses showed a nearly constant chlorine value for hydrolyzable chlorine. In no instance was it necessary to maintain the heating for more than 48 hours. The amount of chloride or bromide ion present in the reaction product was determined by a Volhard titration.

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<sup>1</sup>Shriner and Fuson, "Systematic Identification of Organic Compounds," John Wiley & Sons, New York, 1940, p. 119.



## PART II

### BROMINE OXIDE IN BROMINATION REACTIONS

#### INTRODUCTION

The profound effect of oxygen on the photo-bromination of hydrocarbons has been amply demonstrated. For example, the side-chain bromination of toluene is much more rapid in the presence of small concentrations of oxygen than in the absence of that element.<sup>1</sup> However, as the oxygen pressure is increased, the rate of this bromination goes through a maximum. A similar maximum for the catalytic effect of oxygen has been observed in the bromination of cyclohexane and of methyl cyclohexane. The bromination of isobutane is also catalyzed by oxygen, but, in this instance, the reaction rate increases monotonically with increasing oxygen pressure; there is no maximum rate within the range studied.<sup>2</sup>

Peroxides strongly catalyze the side-chain bromination of toluene, but do not influence the rates of bromination of methyl cyclohexane and isobutane.<sup>3</sup> However, the similarity between the mechanisms of all of the reactions cited is brought out by the fact that small amounts of organic inhibitors retard each of them.

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<sup>1</sup>Kharasch, White and Mayo, J. Org. Chem., **3**, 33 (1938).

<sup>2</sup>Kharasch, Hered and Mayo, J. Org. Chem., **6**, 818 (1941); Hered, Ph.D. Dissertation, Department of Chemistry, University of Chicago, 1939.

<sup>3</sup>Kharasch, Hered and Mayo, op. cit.

## DISCUSSION OF THEORY

The facts just stated may be explained by assuming that all the brominations cited proceed by the chain mechanism indicated by the following equations:



The side-chain bromination of toluene is much more rapid than that of the other hydrocarbons discussed. It has been suggested<sup>1</sup> that the slower reaction of aliphatic hydrocarbons is due to shorter chain lengths rather than to the initiation of a smaller number of chains. This suggestion is compatible with the failure of small amounts of peroxides to increase materially the rate of bromination of aliphatic compounds. The proportion of product resulting from the initiation of short chains by catalytic amounts of peroxide would be undetectable by the methods which have been used. Furthermore, the side-chain bromination of toluene should be more rapid, and the chains should be of much greater length because the benzyl radical formed as an intermediate in reaction (b) is stabilized by resonance.

It is significant that, in bromination reactions, the simultaneous effects of oxygen and light are less comparable with the sum than with the product of their individual effects.<sup>2</sup> Visible light, which is absorbed neither by oxygen nor by the hydrocarbons present, catalyzes these reactions. It must, therefore, be the bromine which renders the reaction mixture light-sensitive. Light probably initiates the reaction chains by dis-

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<sup>1</sup>Kharasch, White and Mayo, J. Org. Chem., 3, 33 (1938).

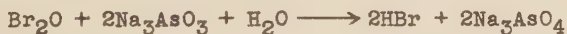
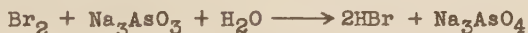
<sup>2</sup>Kharasch, Hered and Mayo, op. cit.

sociating bromine into atoms. Oxygen may serve to increase the average length of these chains, whereas peroxides have no such effect. Conceivably one of the oxides of bromine,  $\text{BrO}_2$  or  $\text{Br}_2\text{O}$ , may be formed as an intermediate and might act as a direct brominating agent.

The present work was undertaken to show qualitatively whether or not the bromine oxide,  $\text{Br}_2\text{O}$ , catalyzes the bromination of toluene and cyclohexane.

#### DISCUSSION OF EXPERIMENTAL RESULTS

By treating carbon tetrachloride solutions of bromine with mercuric oxide under controlled conditions, it is possible to convert as much as 50% of the bromine present to bromine oxide ( $\text{Br}_2\text{O}$ ).<sup>1</sup> The solutions thus obtained may contain as much as 0.05 moles of bromine oxide per liter. The concentrations of bromine oxide can be estimated by comparing the total bromine content of the solution with its oxidizing power. The reactions of bromine and bromine oxide with a reducing agent (e.g., sodium arsenite) are essentially as follows:



Thus, when one mole of either bromine or bromine oxide is reduced, two moles of hydrobromic acid are obtained; the bromine oxide, however, requires for complete reduction twice as much reducing agent as does the bromine. From this difference the amount of bromine oxide present in the solution may be determined.

Brenschede and Schumacker<sup>2</sup> have stated that phosgene is

<sup>1</sup>Brenschede and Schumacker, Z. anorg. Chem., 226, 370 (1936).

<sup>2</sup>Ibid.

formed when carbon tetrachloride solutions of bromine oxide are illuminated; their evidence, however, is far from conclusive. In the course of the present work, the formation of phosgene under the conditions cited was established. Excess bromine was removed from the solution by treating it with cyclohexene. Then nitrogen was passed through the solution. Treatment of the effluent gas with aniline gave a considerable amount of sym-diphenyl-urea.

The following table summarizes the results showing the

EFFECT OF  $\text{Br}_2\text{O}$  ON BROMINATION OF HYDROCARBONS

| Reactants <sup>a</sup> | Original Conc.<br>of $\text{Br}_2\text{O}$ | Illumi-<br>nation <sup>b</sup> | Time for<br>Decolorization |
|------------------------|--------------------------------------------|--------------------------------|----------------------------|
| Toluene                | 0                                          | +                              | 2 minutes                  |
|                        | .002 M                                     | +                              | 4 minutes                  |
|                        | .05 M                                      | +                              | 60 minutes                 |
|                        | .05 M                                      | —                              | >2 weeks                   |
|                        | 0                                          | —                              | >2 weeks                   |
| Cyclohexane            | 0                                          | +                              | 5 hours                    |
|                        | .002 M                                     | +                              | 5 hours                    |
|                        | .05 M                                      | +                              | 5 hours                    |
|                        | .05 M                                      | —                              | >2 weeks                   |
|                        | 0                                          | —                              | >2 weeks                   |

<sup>a</sup>Total bromine content 0.2 molar (calculated as  $\text{Br}^-$ ).  
Initial concentration of hydrocarbon ca. 0.5 molar.

<sup>b</sup>60 watt incandescent lamp at 10 cm.

influence of bromine oxide upon the bromination of toluene and cyclohexane. The reactions by which these results were obtained were carried out in open test tubes; hence, the effects recorded



apply only to what has been called the "oxygen-catalyzed" reaction. The inhibitory effect of bromine oxide on the photo-bromination of toluene is marked. The rates of all of the dark reactions and of the photo-brominations of cyclohexane are essentially identical and unaffected by the presence of bromine oxide.

When either toluene or cyclohexane was mixed in the dark with a solution of carbon tetrachloride containing both bromine and bromine oxide, the bromine oxide rapidly disappeared. Titrations (of the type already described) showed that all of this substance was used up within two minutes. Whatever effect the bromine oxide exerted in the later stages of the reaction (which lasted one to two hours) must, therefore, be attributed to the products formed by this rapid initial reaction.

An attempt was made to isolate carbon compounds containing oxygen which might have been formed by the reaction of bromine oxide on the hydrocarbon. Unreacted bromine and excess solvent were removed from the reaction mixture containing toluene. The yellow concentrate thus obtained inhibited the bromination of more toluene just as did the bromine oxide solution. The yellow coloration could not be removed from the non-aqueous liquid by extraction with water. Aqueous alkali (either hydroxide or carbonate), however, removed the yellow color from the non-aqueous layer; the water layer then rapidly turned dark brown. Acidification of the alkaline solution gave no apparent precipitate, and concentration gave only tarry residues. Tests showed the original concentrate to contain no free bromine; nevertheless, it liberated iodine from acidified potassium iodide and reduced Tollen's reagent instantaneously in the cold. This behavior strongly suggests the presence of a quinone.

All attempts to identify a quinone in the toluene concen-

trate were unsuccessful. However, it was possible to isolate benzoquinone from a similar concentrate of benzene. To secure such a concentrate, benzene was added to the carbon tetrachloride solution in which the bromine oxide was prepared. After the benzoquinone had been removed from the concentrate, the residue still retained its power to liberate iodine from potassium iodide and to reduce Tollen's reagent. No further pure compounds could, however, be isolated from the mixture.

Where cyclohexane was added to the solution in which bromine oxide was prepared, the resulting concentrate was colorless. No carbon compounds containing oxygen were identified. The only product isolated was cyclohexyl bromide.

It has been previously observed<sup>1</sup> that, in brominations carried out in the presence of air, the decolorization (due to the vanishing of free bromine) always starts at the surface and proceeds downward through the solution; experiments in vacuum show uniform decolorization throughout the entire reaction mixture. All of the photo-brominations carried out in the present investigation exhibited decolorization of the first type. These phenomena indicate that the small amount of oxygen originally uniformly distributed throughout the solution is irreversibly consumed in the course of the reaction. Only by diffusion of free oxygen from the air does the so-called "oxygen-catalyzed" reaction proceed. Very probably the effect of the oxygen is due to its destructive action on some inhibitor present.

#### EXPERIMENTAL PART

Materials used.-- Commercial grades of toluene, benzene and cyclohexane were each shaken with concentrated sulfuric acid

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<sup>1</sup> Kharasch, White and Mayo, op. cit.

for several hours, washed with water, dried over calcium chloride and distilled through a 30 cm. column, packed with a nichrome spiral. The first portion of each distillate was rejected, and the main fraction of each (boiling range  $0.5^{\circ}$ ) was collected and stored in glass-stoppered bottles.

Reagent grade bromine and carbon tetrachloride were used without further purification.

Mercuric oxide was prepared according to the directions of Zintl and Rienacker.<sup>1</sup> The mercuric oxide was precipitated at  $50^{\circ}$ , and dried at  $110^{\circ}$ .

#### Preparation and Analysis of Bromine Oxide Solutions.--

For the preparation of solutions of bromine oxide, the method of Brenschede and Schumacker<sup>2</sup> was used. The reaction was carried out in an all-glass apparatus consisting of a 200 cc. three-necked flask equipped with a mercury-sealed stirrer and a reflux condenser to the upper end of which a calcium chloride tube was attached. One opening of the flask was used for the introduction of the reagents and for the removal of solution by a tube leading to a sintered glass filter; during the reaction, this opening was closed with a ground glass stopper.

A mixture of 120 cc. of carbon tetrachloride, 3 cc. liquid bromine and 20 grams of mercuric oxide was stirred and kept for 75 minutes at  $45^{\circ}$ . At this point an additional 5 grams of  $\text{HgO}$  was added, and the mixture was cooled to  $-15^{\circ}$  by an ice-salt bath. The solution, after being cooled for 35 minutes, was sucked from the reaction vessel and passed through the sintered glass filter. The clear filtrate was either used at once or stored in a glass-stoppered flask kept in a Dewar flask at  $-23^{\circ}$  (freezing

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<sup>1</sup>Zintl and Rienacker, Ber. 63, 1908 (1930).

<sup>2</sup>Brenschede and Schumacker, op. cit.

point of carbon tetrachloride).

The oxidizing values and bromine contents of such solutions were determined as follows.

Oxidizing value: Exactly 5 ml. of the solution was added to an excess of 5% sodium hydroxide solution. A large excess of standard 0.1 N sodium arsenite solution was added; then the solution was made strongly acid with concentrated hydrochloric acid. (Hypobromite is reduced in alkaline solution and bromate in acid solution.) The excess sodium arsenite present was back-titrated with standard 0.1 N potassium bromate solution. The end point was determined potentiometrically. The use of a half-cell for this purpose may be avoided by employing two polished platinum wire electrodes. One of these is immersed directly in the solution to be titrated; the other is immersed in the same solution but shielded from the main body of the liquid by a capillary glass tube open at both ends. The end point for the titration is easily recognized by a voltage change of the order of 0.2-0.3 volts.

Bromine content: Exactly 5 ml. of bromine-bromine-oxide solution was added to a solution of sodium sulfite which was then acidified with nitric acid. The bromide ion content of the solution thus prepared was determined by a Volhard titration.

The difference between the number of equivalents of sodium arsenite consumed in the determination of oxidation value and the number of equivalents of silver nitrate consumed in the bromide ion determination is twice the number of moles of bromine oxide in 5 ml. of the original solution.

The Bromination Reactions.-- For sets of comparative brominating reactions, various brominating solutions of equal bromine content were used. In some of these solutions all the bromine was

present as such; in others (prepared as already described), part of the bromine was present in the form of bromine oxide. A sample (10 ml.) of the brominating solution was pipetted in subdued light into a test tube, and 0.5 ml. of hydrocarbon was added. Comparative reactions on each hydrocarbon were carried out simultaneously under identical conditions of illumination and temperature. When reactions were carried out in the dark, the tubes stoppered with glass wool plugs were placed in a dark compartment; the occasional rapid inspections necessary were made in subdued light. The reactions under illumination were carried out with a 60 watt incandescent lamp placed 10 cm. away from the tubes.

Formation of Phosgene in Illuminated Solutions of Bromine Oxide in Carbon Tetrachloride.-- A solution of bromine oxide (0.03 molar) in carbon tetrachloride contained in a long, narrow tube was illuminated by a 60 watt bulb 15 cm. away from the tube. Free halogen was removed by dropwise addition of cyclohexene until the solution was colorless. The other volatile products were carried by a stream of dry nitrogen into an aniline-carbon tetrachloride solution. The white solid which separated was collected on a filter and washed first with dilute hydrochloric acid and finally with water; it was then dried in a dessicator over calcium chloride. The solid melted at  $236^{\circ}$  (uncorrected); sym-diphenylurea is reported to melt at  $238^{\circ}$ - $239^{\circ}$ .<sup>1</sup>

Reaction of Bromine with Mercuric Oxide in the Presence of Hydrocarbons.-- The apparatus was the same as that used for preparation of bromine oxide solutions, but the procedure was modified. Mercuric oxide (45 grams = 0.2 moles), 50 cc. of hydrocarbon (0.5-0.6 moles), and 50 cc. of carbon tetrachloride

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<sup>1</sup>Lange, "Handbook of Chemistry," Handbook Publishers, Inc., Sandusky, O., 4th Ed., 1941, p. 366.



were heated to 50° and stirred. A solution containing 6.9 cc. of bromine (ca. 0.14 moles) in 50 cc. of carbon tetrachloride was added dropwise over a period of about one hour. The mixture was maintained at 50° for about five hours, then cooled to -15°, and maintained at that temperature for about one-half hour. (This procedure removes from the solution mercuric bromide which is quite soluble at higher temperatures.) The solution was filtered in the manner described for the preparation of bromine oxide solution. The solvent together with the unreacted bromine and hydrocarbon were removed from the filtrate by distillation at 100 mm. from an all-glass apparatus equipped with a 30 cm. Vigreux column. At no time was the temperature of the still-pot raised above 50°. The procedure described was used in reactions involving benzene, toluene and cyclohexane. The operations were carried out for the most part in complete darkness; subdued light was used for the necessary visual inspections.

The residue which remained after the removal of the solvent and unreacted materials from the solution containing benzene was a bright yellow viscous oil. This oil liberates iodine from acidified potassium iodide solution and reduces Tollen's reagent instantly in the cold. A portion of the oil was placed at a pressure of 20 mm. in an all-glass apparatus equipped with a cold-finger. Yellow needles sublimed onto the cold-finger. These crystals, after they had been pressed on filter paper, melted at 111°-113° (uncorrected); the material did not depress the melting point of an authentic sample of p-benzoquinone (melting point 114°). The residue remaining after the sublimation of the p-benzoquinone was heated to 40° and kept for several hours at 10 mm. The remaining red, viscous, tacky oil still reduced Tollen's reagent and liberated iodine from potassium iodide. Attempts to isolate

other compounds from this oil were unsuccessful. A considerable portion of the oil appeared to be moderately soluble in water in which it formed pink solutions. It was apparently insoluble in petroleum ether, even at 37°. Aqueous solutions of the oil were decolorized only by several successive extractions with diethyl ether; the resulting ether solutions were yellow rather than pink. The properties here recorded suggested that the oil may have contained o-benzoquinone, but attempts to isolate a derivative of this compound by treating the oil with o-phenylenediamine were unsuccessful.

The residue which remained after the removal of the solvent and unreacted materials from the solution containing toluene showed qualitatively the same behavior as that just described. Attempts to isolate toluquinone from the mixture were, however, unsuccessful.









